An Evaluation of Atmospheric-pressure Plasma for the Cost-Effective Deposition of Antireflection Coatings

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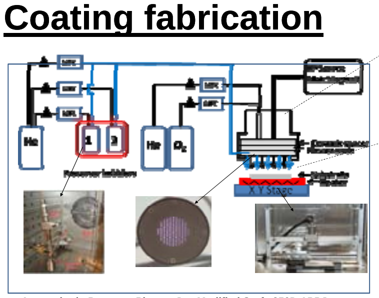
Background

Atmospheric-pressure plasma deposition (APPD) has previously been used to deposit various functional materials including polymeric surface modification layers, transparent conducting oxides, and photo catalytic materials. For many plasma polymerized coatings, reaction occurs via free radical mechanism where the high energy electrons from the plasma activate the olefinic carbon-carbon double bonds - a typical functional group in such precursors. The precursors for such systems are typically inexpensive and readily available and have been used in vacuum PECVD previously.

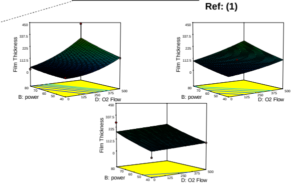
Objectives

- To investigate the effect of plasma power, gas composition and substrate temperature on the Si-based film properties using triethylsilane(TES) as the precursor.
- The chemical, mechanical, and optical properties of several experimental matrices based on Design of Experiment (DOE) principals.

Coating fabrication



Atmospheric Pressure Plasma Jet -Modified Surfx 250D APPJ system



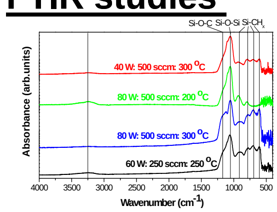
Film thickness Vs deposition conditions

Design of Experiment (DoE) Setup

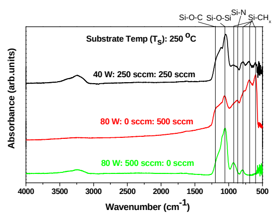
1) Central composite consisting of 4 factors (see table at right).
2) 30 experiments including 5 center points.
3) Constant precursor gas flow (500 SCCM He), plasma gas flow (30 LPM He), and deposition conditions (standoff = 3 mm, deposition speed, etc).

DOE parameters	Plasma Power (Watt)	O_2 (sccm)	N_2 (sccm)	T_s(°C)
Low	40	0	0	200
Medium	60	250	250	250
High	80	500	500	300

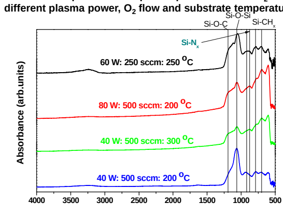
FTIR studies



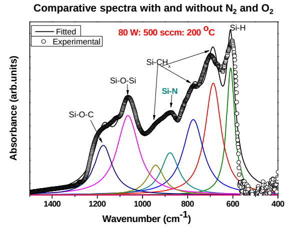
FTIR-ATR spectra of samples deposited without N_2 at different plasma power, O_2 flow and substrate temperature



Comparative spectra with and without N_2 and O_2



FTIR-ATR spectra of samples deposited without O_2 at different plasma power, N_2 flow and substrate temperature



FTIR-ATR deconvoluted spectrum showing the contribution from Si-N bond in the films deposited with N_2 (no O_2).

Peak assignments based on the ref (2)

- Samples deposited with only O_2 flow show prominent Si-O related bonds at higher T_s indicating the SiO formation is driven by substrate conditions rather plasma.
- Significant Si-N bond formation could be observed at higher nitrogen flow (500 sccm) with no oxygen flow.

References:

[1] M. D. Barankin, E. Gonzalez II, A. M. Ladwig, R. F. Hicks, **Sol. Energ. Mat. Sol. C, 91 (2007) 924–930.**

[2] A. M. Wrobel, A. W. Pietrzykowska, M. Ahola, I. J. Vayrynen, **Chem. Vapor. Deposition., 15 (2009) 39-46.**
C. S. Yang, Y. H. Yu, H, J, Lee, K. M. Lee, C. H. choi., **Thin Solid Films., 475 (2005) 150-154.**
J. Dupuis, E. Fourmond, J. F. Lelievre, D. Ballutaud, M. Lemiti, **Thin Solid Films, 516 (2008) 6954-6958.**

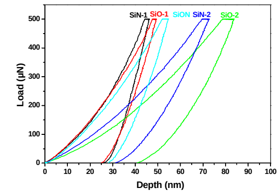
[3] *W. C. Oliver* and G. M. Pharr, **J. Mater. Res., 7 (1992) 1564 – 1583.**

Nano-mechanical properties

(Depth sensitive indentations (DSI))

Sample	Deposition parameter				*H* (GPa)	E_r (GPa)
	Power (Watt)	Gas flow (sccm) N_2	Gas flow (sccm) O_2	T_s (°C)		
SiO-1	40	0	500	200	5.0±0.1	87.2±1.6
SiO-2	80	0	500	300	2.4±0.1	39.7±0.7
SiN-1	40	500	0	200	5.5±0.1	110.3±4.3
SiN-2	80	500	0	200	3.4±0.2	86.7±0.7
SiON	60	250	500	250	4.6±0.1	76.8±2.5
Silicon	--	--	--	--	14.0±04	155.3±2.5

Hardness (*H*) and reduced modulus (E_r) measured using the method of Oliver-Pharr (ref: 3) on films synthesized at different conditions



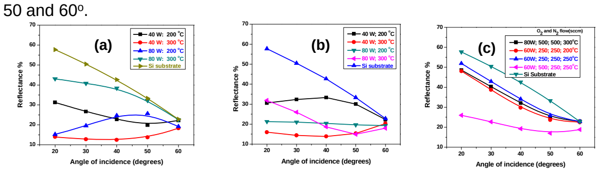
Load- displacement curve of SiC(O/N) thin films

- SiC-O and SiN-O films deposited at 300 °C showed higher hardness.
- SiCON coatings showed mixed properties which strongly depend on the deposition conditions.
- Films deposited at lower T_s showed poor hardness.

Optical studies

Variable Angle Specular Reflectance

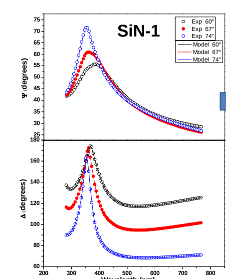
Performed with Cary 5000 UV-Vis-NIR Spectrophotometer at angles: 20, 30, 40, 50 and 60°.



Reflectance spectra of SiC (O/N) coatings: (a) without nitrogen flow; (b) without oxygen flow and (c) with Nitrogen and Oxygen flow, at various plasma powers and T_s

- All the coatings showed reduced reflectance when compared to bare Si substrate, however thickness and refractive index optimization is expected to give a larger range of anti-reflective properties .

Spectroscopic Ellipsometry



MSE : 0.78
Non-uniformity: 6-8 %

Sample	*n*	*K*	Thickness (nm)
SiO-1	1.44	0	140
SiO-2	1.43	0	605
SiN-1	1.54	0	76
SiN-2	1.49	0	440
SiON	1.48	0	183

- Si-N mixed SiO/SiC coatings showed increase in the refractive index.
- Tunability in refractive index by varying composition of the coating.

Summary

- A simple APPD route has been utilized to deposit Si based films from an inexpensive precursor – Triethylsilane (TES).
- Preliminary results indicates formation of Si-C & Si-O and Si-O, Si-C & Si-N bonds with oxygen and nitrogen plasmas respectively. N_2-O_2 plasma showed mixed trend; however oxygen remains a significant portion of all films, despite attempts to minimize exposure to atmosphere.
- SiN, SiC, and SiO ratios can be modified by the reaction conditions resulting in differing film properties.
- SE studies revealed that films with SiN bond possess refractive index higher than coatings with Si-O/Si-C bonds.
- Variable angle reflectance studies showed that SiOCN coatings offer AR properties; however thickness and refractive index optimization of these coatings remains necessary for application as potential AR coatings.

Path Forward

- Deposit selected systems on metalized glass to do I-V, C-V measurements.
- Move deposition system into an inert atmosphere (glove box) and repeat depositions to minimize the level of O_2.
- Investigate alternative precursors and materials for antireflection coatings.

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